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WO 01/95862 A1

(54) Title: **LOW SHRINKING POLYMERIZABLE DENTAL MATERIAL**

(57) Abstract: A low shrinking polymerizable dental material, includes a mixture of a polymerizable di- or poly(meth)acrylate, an alkoxylated bisphenol dimethacrylate, a polymerizable monomer, a polymerization initiator and/or sensitizer, a stabilizer and a filler in a content of 70 to 85 per cent. The volumetric shrinkage during polymerization is less than 2.0 Vol-%.

***Low shrinking polymerizable dental material*****TECHNICAL BACKGROUND**

[0001] Dental filling materials often consist of polymerizable organic monomers and/or polymers, polymerizable monomers, polymerization initiators, and fillers. Known commercial dental composites exhibit useful mechanical properties, such as compressive strengths ranging from 300 to 500 MPa and flexural strengths ranging from 130 to 170 MPa. Furthermore, over the past years they have been improved with respect to abrasion resistance, marginal integrity, fatigue behavior and their optical properties. Nevertheless, a volumetric shrinkage of 2.5 to 4.0% often takes place during the polymerization of these composites. This may cause microfractures in the material and sometimes enamel edge cracks. Frequently, secondary caries are formed as result of these defects. Therefore, it is desirable to provide new composite materials that exhibit reduced volumetric shrinkage without sacrificing other useful properties

[0002] It is known to use 2,2-Bis-[p-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-propane (Bis-GMA) as a monomer for dental materials due to its advantageous properties. However, it shows a relatively high viscosity that makes the application of low viscous monomers necessary. It is known that the shrinkage directly depends on the molecular weight of polymerizable organic monomers. On the other hand, increasing molecular weights of the monomers results in an increasing viscosity of the resin. Therefore, polymerizable monomers, such as oligoethyleneglycol dimethacrylates, are used to obtain a lower viscosity and allows the incorporation of desired amounts of fillers. However, polymerizable monomers show a relatively high shrinkage by themselves, for example 12.89 vol.-% for pure triethyleneglycol dimethacrylate. This leads to a high crosslinking density and brittleness.

[0003] Alkoxyated Bis-GMA's were used as relatively low viscous monomers in content of 15 to 30 % and applied in redox-polymerizable paste-paste composites. Frequently, in combination with other polymerizable monomers ethoxylated or propoxylated Bis-GMA was applied to improve mechanical properties, water sorption and wear resistance. Recently, composites were

used that comprise Urethane dimethacrylates, Triethyleneglycol dimethacrylate 2,2-Bis-[p-(2-hydroxy-3-methacryloyl-oxypropoxy)-phenyl]-propane, and the so called BisEMA6. Another is an ethoxylated Bis-GMA having 6 to 8 ethoxy moieties and it is used in contents of 15 to 45 %. All percents or "%" are by weight (w/w) unless otherwise noted.

**[0004]** Reaction products of diisocyanates and glycerol di(meth)acrylate have been used to prepare a cement composition. Furthermore, compounds have been prepared from vinyl urethane condensate (oxypropylated bisphenol-A), hexamethylene diisocyanate and hydroxypropyl methacrylate.

**[0005]** In US Pat. No. 4,089,763 a method of repairing teeth was described by using a composition comprising particles with a maximum dimension not greater than 500  $\mu\text{m}$  (micrometers or "microns") and a polymerizable prepolymer containing at least two polymerizable ethylenically unsaturated groups being the reaction product of a urethane prepolymer and a polymerizable ethylenically unsaturated monomer.

**[0006]** Special monomers such as tricyclodecane derivatives, polyols, urethane dimethacrylates of diisocyanates and hydroxyalkylmethacrylates show a relatively low volumetric shrinkage which give reason to suppose that the use of monomers with a higher molecular weight would be successful in the application for dental composites.

#### DISCLOSURE OF THE INVENTION

**[0007]** It is therefore, an object of the invention, to provide a low shrinking, polymerizable dental material.

**[0008]** It is another object of the invention to provide such a material useful as a dental restorative material.

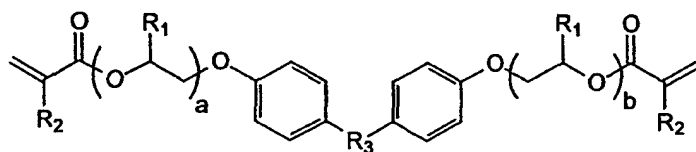
**[0009]** These and other objects of the invention, which shall become apparent from the following description, are achieved by the invention as hereinafter described and claimed.

**[0010]** In general, a low shrinking polymerizable dental material, comprises a mixture of

- (i) 70 to 85 w/w of an organic or an inorganic filler and
  - (ii) 15 to 30 % w/w of a polymerizable resin matrix
- having a volumetric polymerization shrinkage of less than 2 % v/v (by volume). In an alternative embodiment, the material may be a mixture of

- (i) 25 to 40 % w/w of a polymerizable di- or poly(meth)acrylate,
- (ii) 45 to 65 % w/w of an alkoxyated bisphenol dimethacrylate,
- (iii) 0 to 20 % w/w of a polymerizable monomer,
- (iv) 0.1 to 3.0 % w/w of polymerization initiator and/or sensitizer and stabilizer and
- (v) 0 to 10 % w/w of an antimicrobial compound.

In a further embodiment, the alkoxyated bisphenol dimethacrylate can be characterized by the following formula

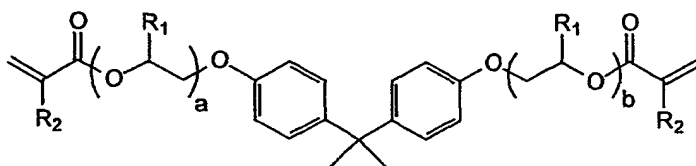


wherein  $R_1$  and  $R_2$  independently denote H (hydrogen) or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene

$R_3$  is a difunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl, O, S,  $SO_2$  or  $C(CF_3)_2$ .

$a$  and  $b$  are integers wherein  $a + b$  is from about 2 to about 20.

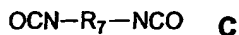
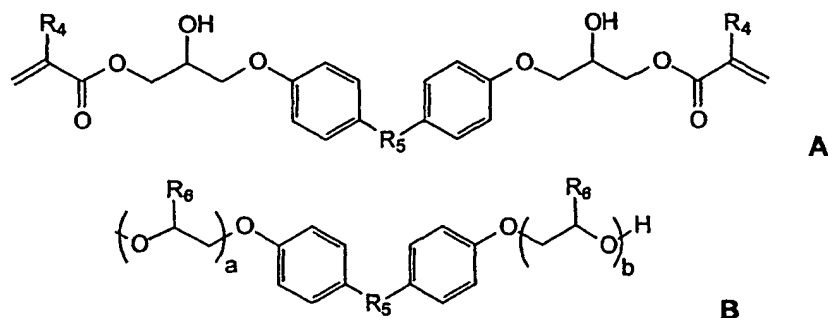
[0011] The alkoxyated bisphenol dimethacrylate may alternatively be characterized by the following formula



wherein  $R_1$  and  $R_2$  independently denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene

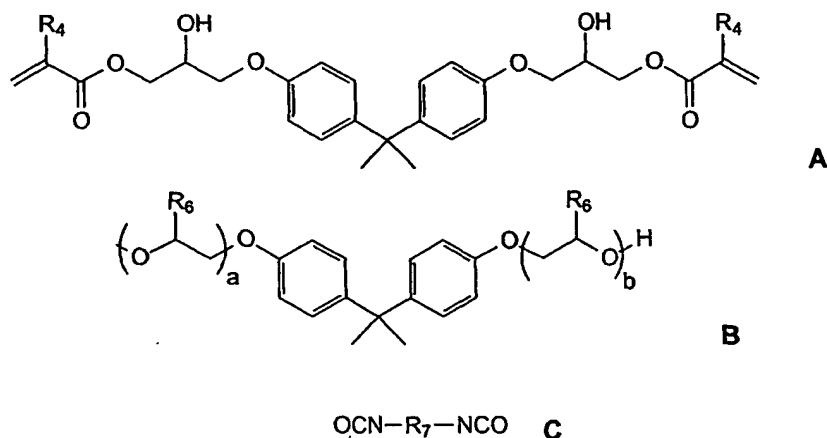
$a$  and  $b$  are integers wherein  $a + b$  is between about 2 and about 20.

[0012] In a still further embodiment, the polymerizable di- or poly(meth)acrylate is the reaction product of molecules A and B with C



whereby the molar ratio of **A** and **B** varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (**A** + **B**) and **C** varies between 1.0 to 0.05 and 1.0 to 1.1, wherein  $\text{R}_4$  denotes H or a monofunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl,  $\text{C}_5$  to  $\text{C}_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene;  $\text{R}_5$  is a difunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl, O, S,  $\text{SO}_2$  or  $\text{C}(\text{CF}_3)_2$ ,  $\text{R}_6$  denotes H or a monofunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl,  $\text{C}_5$  to  $\text{C}_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene  $\text{R}_7$  is a difunctional substituted or unsubstituted  $\text{C}_2$  to  $\text{C}_{30}$  alkylene,  $\text{C}_5$  to  $\text{C}_{30}$  substituted or unsubstituted cycloalkylene, substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene  $a$  and  $b$  are integers.

**[0013]** In a further embodiment, the polymerizable di- or poly(meth)acrylate is formed from the reaction product of molecules **A** and **B** with **C**



[0014] whereby the molar ratio of A and B varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (A + B) and C varies between 1.0 to 0.05 and 1.0 to 1.1,

[0015] wherein  $R_4$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene  $R_6$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene  $R_7$  is a difunctional substituted or unsubstituted  $C_2$  to  $C_{30}$  alkylene,  $C_5$  to  $C_{30}$  substituted or unsubstituted cycloalkylene, substituted or unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene; and, a and b are integers as hereinabove.

[0016] The polymerizable monomer is a mono- or polyfunctional acrylate or methacrylate, such as diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 3,(4),8,(9)-dimethacryloyloxymethyltricyclodecane, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylic- or methacrylic substituted spiroorthoesters, spiroorthocarbonates or bicyloorthoesters, glycerin trimethacrylate, trimethylol propane triacrylate, furfurylmethacrylate.

#### **DESCRIPTION OF THE INVENTION**

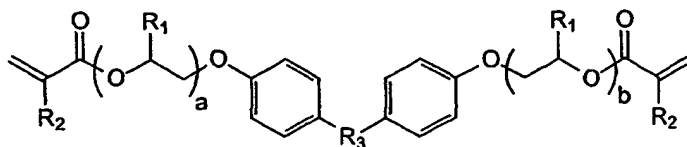
[0017] It has surprisingly been found that a low shrinking polymerizable dental material having a volumetric polymerization shrinkage of less than 2 % v/v is obtainable comprising a mixture of

- (i) 70 to 85 w/w of an organic or an inorganic filler and
- (ii) 15 to 30 % w/w of a polymerizable resin matrix.

[0018] The polymerizable resin matrix comprises a mixture of, for example,

- (i) 25 to 40 % w/w of a polymerizable di- or poly(meth)acrylate,
- (ii) 45 to 65 % w/w of an alkoxyated bisphenol dimethacrylate ,
- (iii) 0 to 20 % w/w of a polymerizable monomer and
- (iv) 0.1 to 3.0 % w/w of polymerization initiator and/or sensitizer and stabilizer.

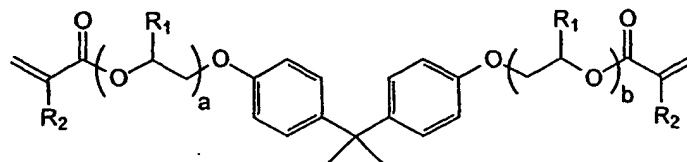
[0019] The alkoxyated bisphenol dimethacrylate may be characterized by the following formula



wherein  $R_1$  and  $R_2$  independently denote H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene;

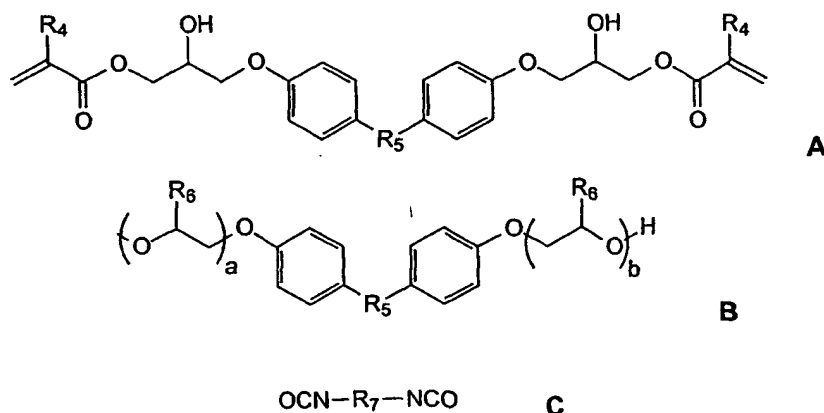
$R_3$  is a difunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl, O, S,  $SO_2$  or  $C(CF_3)_2$ ; and,  $a$  and  $b$  are integers. Preferably  $a + b$  is between 2 and 20, more preferably  $a + b$  is between 8 and 20.

[0020] Preferably the alkoxylated bisphenol dimethacrylate is characterized by the following formula



wherein  $R_1$  and  $R_2$  independently denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene, and  $a$  and  $b$  are integers.

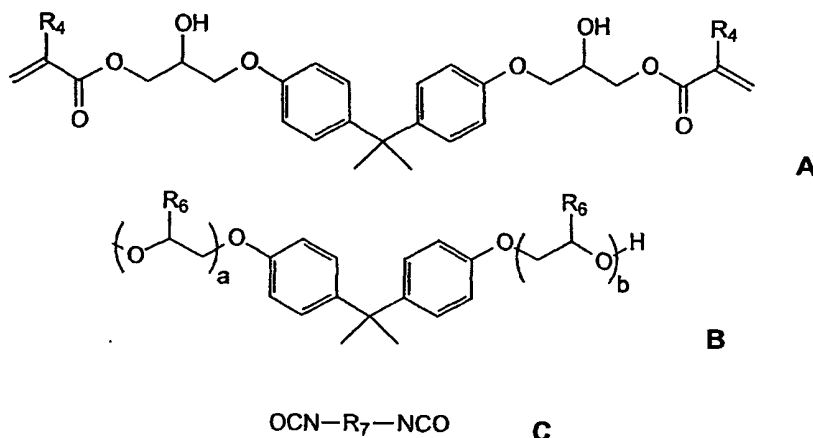
[0021] An example of a useful polymerizable di- or poly(meth)acrylate is the reaction product of molecules **A** and **B** with diisocyanate **C** as follows:



wherein the molar ratio of **A** and **B** varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (**A** + **B**) and **C** varies between 1.0 to 0.05 and 1.0 to

1.1; wherein  $R_4$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene;  $R_5$  is a difunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl, O, S,  $SO_2$  or  $C(CF_3)_2$ ;  $R_6$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene;  $R_7$  is a difunctional substituted or unsubstituted  $C_2$  to  $C_{30}$  alkylene,  $C_5$  to  $C_{30}$  substituted or unsubstituted cycloalkylene, substituted or unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene and a and b are integers as hereinabove.

[0022] In the alternative, the polymerizable di- or poly(meth)acrylate is received by reaction of molecules **A** and **B** with diisocyanate **C**



whereby the molar ratio of **A** and **B** varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (**A** + **B**) and **C** varies between 1.0 to 0.05 and 1.0 to 1.1; wherein  $R_4$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene;  $R_6$  denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene;  $R_7$  is a difunctional substituted or unsubstituted  $C_2$  to  $C_{30}$  alkylene,  $C_5$  to  $C_{30}$  substituted or unsubstituted cycloalkylene, substituted or unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene; and a and b are integers as hereinabove.

[0023] As polymerizable monomers are usable mono- and polyfunctional acrylates or methacrylates, such as diethyleneglycol dimethacrylate,



triethyleneglycol dimethacrylate, 3,(4),8,(9)-dimethacryloyloxymethyl tricyclodecane, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylic- or methacrylic substituted spiroorthoesters, spiroorthocarbonates or bicycloorthoesters, glycerin trimethacrylate, trimethylol propane triacrylate, furfurylmethacrylate.

[0024] The photoinitiator is for example benzoinmethylether, benzilketal, camphor quinone/amine, or an acylphosphin oxide in a content of 0.1 to 3 wt-%, or any other conventional and useful photoinitiator.

[0025] The low shrinking dental material is filled with inorganic fillers, inorganic compounds such as  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{BiPO}_4$ ,  $\text{CaWO}_4$ ,  $\text{BaWO}_4$ ,  $\text{SrF}_2$ ,  $\text{Bi}_2\text{O}_3$ , porous glasses or organic fillers, such as polymer granulate or a combination of organic and/or inorganic fillers or reactive inorganic fillers having a average diameter of less than about 10  $\mu\text{m}$ .

[0026] The volumetric shrinkage was measured using AccuPyc 1300 (Micrometrics, USA) based on measurements of density of polymerized and non-polymerized composite followed by calculation of volumetric shrinkage. This method was applied and described by W.D. Cook et al., Dent. Mat. 15 (1999) 447.

[0027] The Archimedes method for estimation of the shrinkage bases on the measurement of the weight of the non-polymerized and of the polymerized material on air and in water. From these values the densities are calculated. The densities of the non-polymerized and of the polymerized material are used for calculating the shrinkage.

### EXAMPLE 1

[0028] 27.864 g 2,2-Bis-[p-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-propane, 61.308 g Ethoxylated Bis-GMA CD540, 2.500 g Diethylene glycol dimethacrylate and 0.330 Dibutyl tinlaurate were mixed homogeneously under stirring and heating at 40 °C. To this reaction mixture 7.898 g Hexamethylene diisocyanate were added and reacted until the absorption band of isocyanate completely disappeared at 2220  $\text{cm}^{-1}$ .

[0029] Thereafter 0.1 g 2,6-di-tert.-butyl-4-cresol, 0.300 g camphor quinone and 0.350 g Dimethyl aminobenzoic acid ethylester were dissolved in the polymerizable matrix resin. This resin has a viscosity at 23 °C of  $57.3 \pm 0.8$  Pa\*s and a refractive index at 20 °C of 1.5360.

[0030] Using 24.350 g polymerizable matrix resin and 75.650 g Barium aluminosilicate glass a composite was prepared by mixing and stirring under vacuum.

[0031] The properties of the composite are summarized in Table 1.

#### **EXAMPLE 2**

[0032] 20.898 g 2,2-Bis-[p-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-propane, 63.395 g Ethoxylated Bis-GMA (CD540 Sartomer), 4.681 g Bisphenol-A-propoxylate (1PO/Phenol), 2.500 g Diethylene glycol dimethacrylate and 0.330 Dibutyl tinlaurate were mixed homogeneously under stirring and heating at 40 °C. To this reaction mixture 7.898 g Hexamethylene diisocyanate were added and reacted until the absorption band of isocyanate completely disappeared at 2220 cm<sup>-1</sup>.

[0033] Thereafter 0.1 g 2,6-di-tert.-butyl-4-cresol, 0.300 g camphor quinone and 0.350 g Dimethyl aminobenzoic acid ethylester were dissolved in the polymerizable matrix resin. This resin has a viscosity at 23 °C of 48.6 ± 0.2 Pa\*s, a refractive index at 20 °C of 1.5361 and a volumetric shrinkage  $\Delta V (A) = 4.15 \%$ .

[0034] Using 24.560 g polymerizable matrix resin and 75.440 g Barium aluminosilicate glass a composite was prepared by mixing and stirring under vacuum.

[0035] The properties of the composite are summarized in Table 1.

#### **COMPARATIVE EXAMPLES 1 - 10**

[0036] In the following are summarized the results of shrinkage measurement using AccuPyc 1330 of commercial composites as well as their mechanical properties.

Table 1 Properties of claimed and competitive composites

Composite	Producer	Batch	Color	Polymerization $\Delta V$ *) %	Compressive strength MPa	Flexural strength MPa	E-modules MPa
Example 1	Dentsply	MG3-148-1	non-colored	$1.854 \pm 0.046$	$342 \pm 14$	$119 \pm 14$	$8000 \pm 592$
Example 2	Dentsply	MG3-159-3	non-colored	$1.501 \pm 0.102$	$307 \pm 18$	$133 \pm 10$	$7574 \pm 748$
Synergy	Coltene	IB741	A2	$2.683 \pm 0.105$	$343 \pm 19$	$114 \pm 4$	$7590 \pm 280$
Spectrum	Dentsply	00591	A2	$3.156 \pm 0.105$	$325 \pm 21$	$101 \pm 5$	$8174 \pm 292$
Z100	3M	19980130	A2	$2.305 \pm 0.125$	$403 \pm 23$	$135 \pm 4$	$12219 \pm 554$
Herculite	Kerr	904125	C2	$2.475 \pm 0.096$	$337 \pm 30$	$110 \pm 7$	$7790 \pm 328$
Prodigy	Kerr	906417	A2	-	$352 \pm 34$	$120 \pm 10$	$6880 \pm 194$
Prodigy cond.	Kerr	910154	A2	$2.759 \pm 0.020$	$355 \pm 19$	$96 \pm 8$	$7159 \pm 421$
Solitaire	Kulzer	29	A20	$3.096 \pm 0.114$	$382 \pm 20$	$56 \pm 6$	$3789 \pm 363$
Charisma	Kulzer	60026	A2	$3.253 \pm 0.129$	$3565 \pm 16$	$98 \pm 14$	$7491 \pm 274$
Tetric Ceram	Vivadent	B10473	A2	$2.491 \pm 0.048$	$343 \pm 21$	$125 \pm 4$	$8822 \pm 280$
Ariston pHc	Vivadent	B21134	universal white	$2.539 \pm 0.180$	$309 \pm 12$	$97 \pm 8$	$8076 \pm 512$

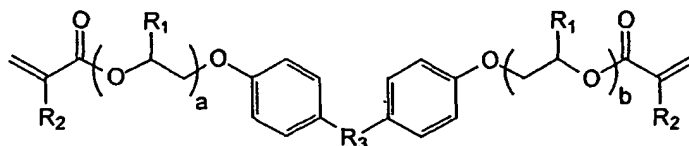
\*) Measurement of density of polymerized and non-polymerized composite using AccuPyc 1330 followed by calculation of volumetric shrinkage

[0037] It should now be apparent that a dental material according to the foregoing description accomplishes the objects of the invention and otherwise makes a contribution to the art. The foregoing description illustrates preferred embodiments of the invention. However, concepts employed may, based upon the description, be employed in other embodiments without departing from the scope of the invention.

**We claim:**

**We claim:**

1. Low shrinking polymerizable dental material, comprising a mixture of
  - (iii) 70 to 85 w/w of an organic or an inorganic filler and
  - (iv) 15 to 30 % w/w of a polymerizable resin matrix
 having a volumetric polymerization shrinkage of less than 2 % v/v.
2. Low shrinking polymerizable dental material of claim 1, wherein said polymerizable resin matrix comprising a mixture of
  - (vi) 25 to 40 % w/w of a polymerizable di- or poly(meth)acrylate,
  - (vii) 45 to 65 % w/w of an alkoxyated bisphenol dimethacrylate,
  - (viii) 0 to 20 % w/w of a polymerizable monomer,
  - (ix) 0.1 to 3.0 % w/w of polymerization initiator and/or sensitizer and stabilizer and
  - (x) 0 to 10 % of an antimicrobial compound.
3. Low shrinking polymerizable dental material of claims 2, wherein said alkoxyated bisphenol dimethacrylate is characterized by the following formula



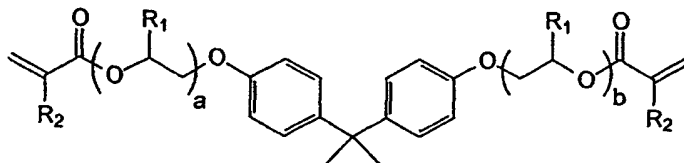
wherein

$R_1$  and  $R_2$  independently denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene

$R_3$  is a difunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl, O, S,  $SO_2$  or  $C(CF_3)_2$ ,

a and b are integers.

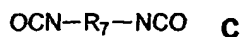
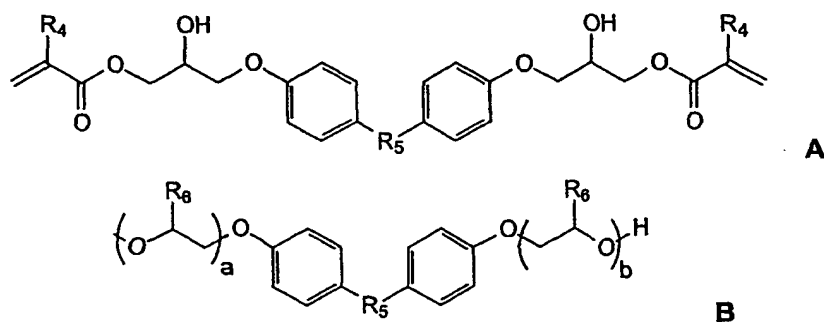
4. Low shrinking polymerizable dental material of claim 3, wherein preferably  $a + b$  is ranging between 2 and 20.
5. Low shrinking polymerizable dental material of claim 3, wherein  $a + b$  is from 8 to 20.
6. Low shrinking polymerizable dental material of claim 2, wherein said alkoxyated bisphenol dimethacrylate is characterized by the following formula



wherein

$R_1$  and  $R_2$  independently denotes H or a monofunctional substituted or unsubstituted  $C_1$  to  $C_{18}$  alkyl,  $C_5$  to  $C_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $C_5$  to  $C_{30}$  arylene or heteroarylene  
 $a$  and  $b$  are integers.

7. Low shrinking polymerizable dental material of claim 6, wherein  $a + b$  is from 2 to 20.
8. Low shrinking polymerizable dental material of claim 6, wherein  $a + b$  is from 8 to 20.
9. Low shrinking polymerizable dental material of claim 2, wherein said polymerizable di- or poly(meth)acrylate is the reaction product of molecules **A** and **B** with **C**



wherein the molar ratio of **A** and **B** varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (**A** + **B**) and **C** varies between 1.0 to 0.05 and 1.0 to 1.1,

wherein

$\text{R}_4$  denotes H or a monofunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl,  $\text{C}_5$  to  $\text{C}_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene

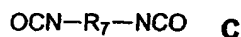
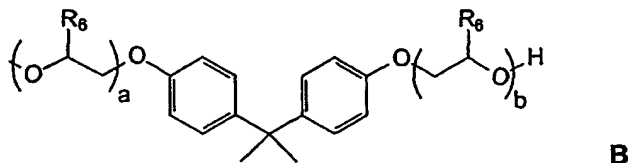
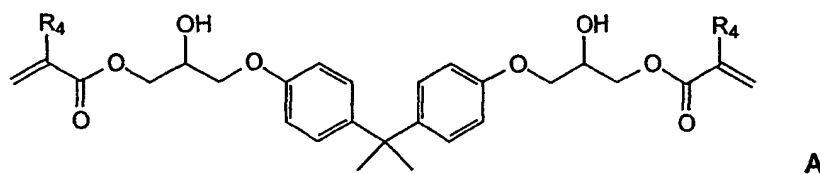
$\text{R}_5$  is a difunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl, O, S,  $\text{SO}_2$  or  $\text{C}(\text{CF}_3)_2$ ,

$\text{R}_6$  denotes H or a monofunctional substituted or unsubstituted  $\text{C}_1$  to  $\text{C}_{18}$  alkyl,  $\text{C}_5$  to  $\text{C}_{18}$  substituted or unsubstituted cycloalkyl, substituted unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene

$\text{R}_7$  is a difunctional substituted or unsubstituted  $\text{C}_2$  to  $\text{C}_{30}$  alkylene,  $\text{C}_5$  to  $\text{C}_{30}$  substituted or unsubstituted cycloalkylene, substituted or unsubstituted  $\text{C}_5$  to  $\text{C}_{30}$  arylene or heteroarylene

$a$  and  $b$  are integers.

10. Low shrinking polymerizable dental material of claim 2, wherein said polymerizable di- or poly(meth)acrylate is received by reaction of molecules **A** and **B** with **C**



whereby the molar ratio of **A** and **B** varies between 1.0 to 0 and 0.2 to 0.8 and the molar ratio of (**A** + **B**) and **C** varies between 1.0 to 0.05 and 1.0 to 1.1,

wherein

R<sub>4</sub> denotes H or a monofunctional substituted or unsubstituted C<sub>1</sub> to C<sub>18</sub> alkyl, C<sub>5</sub> to C<sub>18</sub> substituted or unsubstituted cycloalkyl, substituted unsubstituted C<sub>5</sub> to C<sub>30</sub> arylene or heteroarylene

R<sub>6</sub> denotes H or a monofunctional substituted or unsubstituted C<sub>1</sub> to C<sub>18</sub> alkyl, C<sub>5</sub> to C<sub>18</sub> substituted or unsubstituted cycloalkyl, substituted unsubstituted C<sub>5</sub> to C<sub>30</sub> arylene or heteroarylene

R<sub>7</sub> is a difunctional substituted or unsubstituted C<sub>2</sub> to C<sub>30</sub> alkylene, C<sub>5</sub> to C<sub>30</sub> substituted or unsubstituted cycloalkylene, substituted or unsubstituted C<sub>5</sub> to C<sub>30</sub> arylene or heteroarylene

a and b are integers.

11. Low shrinking polymerizable dental material of claim 2 wherein said polymerizable monomer is a mono- and polyfunctional acrylate or methacrylate.
12. Low shrinking polymerizable dental material of claim 11, wherein said monomer is diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 3,(4),8,(9)-dimethacroyloxymethyltricyclodecane, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylic- or methacrylic substituted



spiroorthoesters, spiroorthocarbonates or bicyloorthoesters, glycerin trimethacrylate, trimethylol propane triacrylate, furfurylmethacrylate.

13. Low shrinking polymerizable dental material of claim 2 wherein said polymerization initiator and/or sensitizer is photoinitiator selected from benzoinmethylether, benzilketol, camphor quinone or acylphosphinoyl.
14. Low shrinking polymerizable dental material of claim 2 wherein the polymerization initiators is a redox initiator selected from dibenzoylperoxide/aromatic or aliphatic tert. amine, tert. butyl peroxy benzoate/ascorbic acid/metal compound.
15. Low shrinking polymerizable dental material of claim 1 wherein said filler is an inorganic filler, an inorganic compound such as  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{BiPO}_4$ ,  $\text{CaWO}_4$ ,  $\text{BaWO}_4$ ,  $\text{SrF}_2$ ,  $\text{Bi}_2\text{O}_3$ , a porous glass or an organic filler, such as polymer granulate or a combination of organic and/or inorganic fillers or reactive inorganic fillers.
16. Low shrinking polymerizable dental material of claim 1 wherein said filler are embrittled glass fibers or compositions of these fillers and inorganic and/or organic fillers.
17. Low shrinking polymerizable dental material of claim 1 wherein said antimicrobial compound is a antimicrobial acting substance selected from trichlosan or chlorohexidine.

## INTERNATIONAL SEARCH REPORT

In ... nal Application No

F ... S 01/18930

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 A61K6/083

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 43596 A (DENTSPLY INT INC) 8 October 1998 (1998-10-08)	1-11, 13, 14
Y	page 14, last paragraph - page 17, paragraph 1 page 18, paragraph 2 claims; examples	12, 15, 17
Y	EP 0 951 894 A (DENTSPLY DETREY GMBH) 27 October 1999 (1999-10-27) page 7, line 35 - line 42	12, 15
Y	WO 98 48766 A (DENTSPLY INT INC) 5 November 1998 (1998-11-05) page 8, paragraph 1 - paragraph 2 claims; example 2	17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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\*G\* document member of the same patent family

Date of the actual completion of the international search

5 November 2001

Date of mailing of the international search report

13/11/2001

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## INTERNATIONAL SEARCH REPORT

In — — — — — Application No

PCT/US 01/18930

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 853 939 A (JENERIC PENTRON INC) 22 July 1998 (1998-07-22) page 3, line 39 -page 5, line 51 -----	1-3,11, 13-15
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Information on patent family members

International Application No

PCT/JP 01/18930

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